

Retention model for ion-pair chromatography based on double-layer ionic adsorption and exchange*

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Abstract: Previous work has demonstrated the validity of an electrical double-layer model for sorption of sample ions onto low capacity ion exchangers. In the present work it is shown how this model can be used in describing the chromatographic retention of sample ions in so-called reversed-phase ion-pair chromatography. The pairing ion added to the mobile phase is sorbed onto the reversed-phase sorbent, creating an electrical double layer and a surface electrical potential ψ_0 . Sample counterions undergo both ion exchange for electrolyte ions in the diffuse part of the double layer and surface adsorption. The latter depends on the magnitude of ψ_0 , which can be calculated from the Stern–Gouy–Chapman theory. The model predicts virtually all of the phenomena that have been described in the literature on ion-pair chromatography.

Keywords: *Ion-pair chromatography; electrical double layer; ionic retention.*

Introduction

The technique usually referred to as ‘ion-pair chromatography’ or ‘reversed-phase ion-pair chromatography’ has become the most commonly used high-performance liquid chromatographic (HPLC) technique for the analytical determination of ionic sample components [1–3]. This has, naturally, stimulated interest in the chemical processes underlying the technique. However, in spite of the many studies that have been directed towards developing a physico-chemical model to explain the sorption of sample ions onto reversed-phase packings from mobile phases containing relatively large oppositely charged ions (pairing ions), there is by no means universal agreement on the subject. A number of models or so-called ‘mechanisms’ have been advanced [2–22].

Several years ago a series of fundamental studies were initiated in the author’s laboratory, the ultimate goal being the development of a physico-chemical model for ion-pair retention on reversed-phase sorbents. The strategy has been to elucidate

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systematically, in a step-by-step fashion, the individual component processes which take place in an ion-pair chromatographic system and then, with these understood, subsequently to address the overall system. Hence, rather than start with a system composed of a silica-based C_{18} -bonded phase sorbent, an aqueous–organic mobile phase, an ion-pairing reagent and a sample ion, the first stage in this program was a study of the sorption of a large organic cation from aqueous solution onto the non-ionic, polymeric sorbent Amberlite XAD-2 [23, 24]. This nonpolar, styrene-divinylbenzene macroporous adsorbent was used as the reversed-phase sorbent in preference to a silica-based alkyl-bonded phase because it possesses a homogeneous, rather well defined surface which is relatively free of strong adsorption sites such as the free-silanol sites found on silica-based sorbents [21, 25, 26].

In this first study it was demonstrated that the sorption of diphenylguanidinium ($DPGH^+$) cation onto XAD-2 could be quantitatively explained by a model based on the well-known Stern–Gouy–Chapman (SGC) theory of the electrical double layer. According to the nomenclature of SGC theory the $DPGH^+$ is described as the potential determining ion, while in the context of ion-pair chromatography it can be considered as the pairing ion.

In the second stage of the program, XAD-2 was converted into a low capacity ion exchanger. Both an anion exchanger (QXAD) and a cation exchanger (SXAD) were made by covalently binding, respectively, either quaternary ammonium groups or sulphonate groups to the surface phenyl groups [27–29]. Only a small fraction of the surface phenyl groups were derivatized so that QXAD and SXAD continued to act as adsorbents. It was demonstrated that the sorption of oppositely-charged sample ions (counterions) from aqueous solution is quantitatively described by a model involving both *ion exchange* in the diffuse part of the electrical double layer and *surface adsorption* onto the electrically charged surface — the latter being described in terms of SGC theory. Mathematical derivations of the equations for this model have been published [29, 30].

In the context of ion-pair chromatography the covalently bound quaternary ammonium groups and sulphonate groups on QXAD and SXAD, respectively, are analogous to the pairing ion, with the important difference that in this case the pairing ion has not been adsorbed on to the surface from the mobile phase but rather is permanently attached, so that its surface concentration does not vary with changes in mobile phase composition.

To summarize, using the terminology of ion-pair chromatography, the first study described above characterized the dependence of *pairing ion sorption* on mobile phase composition, while the second study characterized the dependence of *sample ion sorption* on mobile phase composition under conditions where the amount of pairing ion on the stationary phase is forced to be constant, independent of mobile phase composition. It is the purpose of the present paper to show how the information obtained in these studies can be used to devise a retention model for sample ions in ion-pair chromatographic systems. In these systems the sorption of *both* pairing ion and oppositely charged sample ion depends on mobile phase composition. Moreover, the sorption of sample ion depends on the amount of sorbed pairing ion. It is relevant to point out that it is now well established that the pairing ion is sorbed onto alkyl-bonded phases in ion-pair chromatography and also that Deelder [31] has already demonstrated that the sorption of a pairing ion onto a C_{18} -bonded phase can be described in terms of SGC theory.

Theory

In the following discussion the ion-pair reagent added to the mobile phase is designated as PCl, where the organic cation P^+ is the pairing ion. The sample ion is an hypothetical organic anion S^- , which is injected into the chromatographic column as its sodium salt NaS. In addition to water, ion-pair reagent and sample compound, the mobile phase also contains an inert electrolyte NaCl. No organic modifier such as methanol is present, although this point is raised below in the Discussion. For illustration, DPGH⁺ will be considered to be the pairing ion P^+ .

Sorption of P^+

Sorption isotherms for P^+ (i.e. DPGH⁺) on the reversed-phase packing XAD-2 are shown in Fig. 1 [23], which presents plots of experimentally measured surface excess of sorbed P^+ (Γ_P , moles cm^{-2}) vs solution concentration of P^+ ($[P^+]$, moles/l), at various molar concentrations of added NaCl. The P^+ is adsorbed on to the XAD-2 surface by chemical forces such as π - π dispersion interactions, which may include a substantial entropy contribution, and creates a positive surface-charge. Because electroneutrality must be maintained in the region of the sorbent-solution interface, there must exist in the solution near the interface a surface excess of negative charge that is stoichiometrically equivalent to the surface charge density of P^+ . This region of negative charge is not a thin plane like that of the P^+ charge-surface, but is rather described as a relatively thick region, usually tens or more Ångstrom units thick, called the 'diffuse-part' of the electrical double layer. The region of solution well removed from the interface, where there is no excess negative charge, is described as the bulk solution.

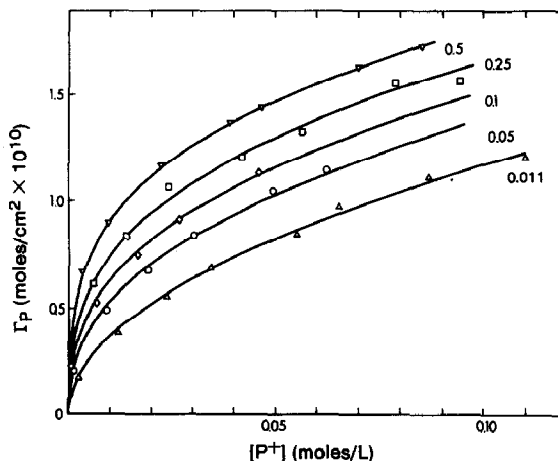


Figure 1
Experimentally measured adsorption isotherms for P^+ . The number by each curve indicates the concentration (mol/l) of added NaCl.

The surface charge density, σ_o in coulomb cm^{-2} , is related to the adsorbed concentration of P^+ by the expression

$$\sigma_o = Z_+ F \Gamma_P^{\text{AD}} \quad (1)$$

where $Z_+ = +1$, F is the Faraday constant (96 487 coulomb/equivalent) and Γ_P^{AD} is the

surface excess due to the *adsorbed* P^+ . The distinction between Γ_P^{AD} and Γ_P is discussed in the Appendix below.

There are two important consequences of the double-layer structure of the interface: (i) there exists an electrical potential between the charge-surface and the bulk solution whose value can be predicted from SGC theory; and (ii) a 'dynamic' ion exchanger has been created in which adsorbed P^+ ions are analogous to the fixed-charge sites on a conventional ion exchanger and in which the counterions in the diffuse layer (i.e. Cl^-) can be exchanged for S^- counterions in the bulk solution. The ion-exchange capacity, Q_{weight} in milliequivalents per gram, is related to Γ_P by the expression:

$$Q_{weight} = 10^3 A_{SP} \Gamma_P \quad (2)$$

where A_{SP} is the specific surface area of the packing ($3.5 \times 10^6 \text{ cm}^2 \text{ g}^{-1}$ for XAD-2). The use of Γ_P rather than Γ_P^{AD} when discussing ion exchange is related to the choice of bulk solution concentration as a reference for defining surface excess and is discussed in the Appendix. It is important to recognize that, unlike a conventional ion exchanger in which the fixed-charge sites are covalently bound to the matrix, the ion-exchange capacity of a 'dynamic' ion exchanger varies in direct proportion to Γ_P .

With this picture of the double layer in mind the sorption isotherms for P^+ in Fig. 1, several aspects of which are relevant, can now be considered. First, Γ_P increases with increasing concentration $[P^+]$ in the mobile phase. These isotherms are in fact Langmuirian, though that is incidental. Second, for a constant $[P^+]$ in the mobile phase Γ_P increases, and thus Q_{weight} increases, when the total electrolyte concentration is increased by the addition of an inert electrolyte, NaCl. This is quantitatively predicted from SGC theory [23].

Sorption of sample S^-

Now consider the sorption of S^- by a reversed-phase packing, onto which has already been adsorbed the pairing ion P^+ . For simplicity the following conditions will be specified: (i) only a relatively small fraction of the available sorbent surface is occupied by P^+ ; and (ii) 'trace' conditions of sorption prevail for S^- [27, 28], which means that the amount of S^- sorbed (in moles) is much smaller than that of P^+ , and that the concentration of Cl^- in the mobile phase is much higher than that of S^- . Trace conditions are a prerequisite for a linear distribution isotherm for S^- [27, 28].

The chromatographic capacity factor k'_S for the sorption of S^- is given by two capacity factors — one attributable to the ion exchange of S^- for Cl^- in the diffuse part of the double layer, $k'_{S,IEX}$, and the other to the adsorption of S^- on the surface, $k'_{S,ADS}$:

$$k'_S = k'_{S,IEX} + k'_{S,ADS} \quad (3)$$

The following expressions have been developed based on previous studies [23, 24, 27–30]:

$$k'_{S,IEX} = \frac{-Z_+ A K_{S,IEX} \Gamma_P}{Z_- V_M c} \quad (4)$$

$$k'_{S,ADS} = \frac{10^{-3} A d}{V_M \gamma_{S,ADS}} \cdot \gamma_S \cdot \exp\left[-\frac{Z_- F \psi_0 + \mu_{S,ADS}^0}{RT}\right] \quad (5)$$

in which $Z_- = -1$ for S^- ; $Z_+ = +1$; A is the total surface area of packing in the chromatographic column (cm^2); V_M is the column void volume (l); c is the concentration of Cl^- in bulk solution (i.e. ionic strength, moles/l); d is the thickness of the compact part of the double layer, which is a constant approximately equal to the hydrated radius of the Cl^- ion (3.7×10^{-8} cm); $\gamma_{S,ADS}$ is the activity coefficient of S^- adsorbed on the surface, which will be approximated as 1 (cf Discussion); $\mu_{S,ADS}^{\circ}$ is the standard chemical potential for transfer of S^- from bulk solution to the surface (joule/mol); ψ_0 is the electrical potential of the surface (volt); and $K_{S,IEX}$ is the ion exchange equilibrium constant for the exchange of S^- from bulk solution for Cl^- in the diffuse layer [27–30]. The ionic activity coefficient γ_S of S^- in the mobile phase can be approximated by the Debye–Hückel limiting law, which at 25°C is:

$$\gamma_S \approx 10^{-0.509\sqrt{c}} \quad (6)$$

The first terms on the right-hand side of equations (4) and (5) are constants for a particular combination of chromatographic column, ion-pair reagent and sample ion, as is the chemical potential $\mu_{S,ADS}^{\circ}$.

The value of Γ_P must be measured experimentally as a function of c , where:

$$c = [\text{NaCl}] + [\text{P}^+]. \quad (7)$$

The quantity γ_S is calculated from c through equation (6), and the quantity ψ_0 is calculated from c and Γ_P as discussed below in the Appendix. Values of $K_{S,IEX}$ and $\mu_{S,ADS}^{\circ}$ for the hypothetical S^- will be assumed to have some convenient value for illustrative purposes. In practice, when testing the validity of the proposed retention model experimentally, values of $K_{S,IEX}$ and $\mu_{S,ADS}^{\circ}$ would have to be obtained from the experimental data by a curve-fitting process analogous to that employed in [27] and [28].

Experimental

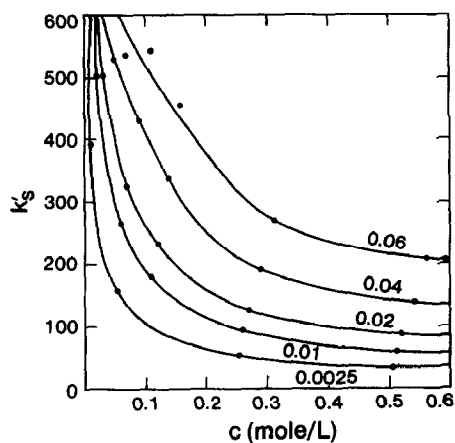
Although this paper is mainly theoretical, the proposed retention model requires the use of experimentally measured sorption isotherms for the pairing ion P^+ . Relatively few studies of pairing-ion sorption isotherms have been performed at several different concentrations of electrolyte c . The experimental data used in the present paper (Fig. 1) are plots of Γ_P vs $[\text{P}^+]$ carried out with five different concentrations of added inert electrolyte, viz 0.011, 0.05, 0.1, 0.25 and 0.5 M NaCl. Although the concentration of inert electrolyte does not greatly exceed the concentration of ion-pair reagent ‘swamping’ conditions are approached at the higher NaCl concentrations.

Two types of hypothetical experiment are described. In the first k'_S is plotted against c at constant $[\text{P}^+]$ in the mobile phase. This corresponds to taking vertical ‘cuts’ through Fig. 1 in order to obtain the appropriate values of Γ_P for use in calculating k'_S . The experiment is repeated for a total of five different values of $[\text{P}^+]$, for which the results are presented in Fig. 2.

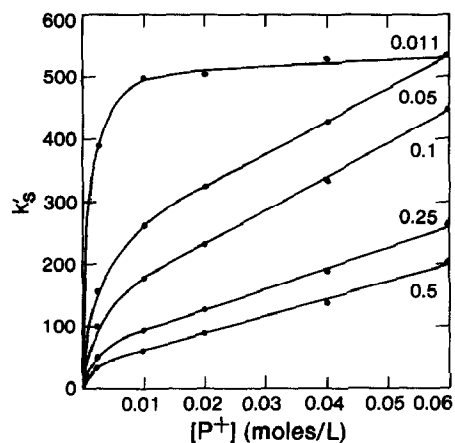
In the second type of experiment, k'_S is plotted vs $[\text{P}^+]$ at a constant concentration of added NaCl; this experiment is repeated for a total of five different values of $[\text{NaCl}]$. This corresponds to moving along each of the isotherms in Fig. 1 in order to obtain the required value of Γ_P . At lower values of $[\text{NaCl}]$ the value of c increases significantly with increasing $[\text{P}^+]$ (equation 7), while at higher $[\text{NaCl}]$ the value of c is more nearly constant as $[\text{P}^+]$ is increased. The results are shown in Fig. 3.

Figure 2

Effect of electrolyte concentration on capacity factor for an hypothetical sample ion S^- at constant pairing-ion concentration. The number by each curve indicates the concentration (mol/l) of pairing ion P^+ in the mobile phase. $K_{S,IEX} = 200$; $\mu_{S,ADS}^0 = -5 \times 10^3$; values of other parameters are as given in the text, adapted from [27].

**Figure 3**

Effect of pairing-ion concentration on capacity factor for an hypothetical sample ion S^- . The number by each curve indicates the concentration (mol/l) of added NaCl. $K_{S,IEX} = 200$; $\mu_{S,ADS}^0 = -5 \times 10^3$; values of other parameters are as given in the text, adapted from [27].



In the illustrative calculations, values of V_M (1.25×10^{-3} l) and A (1.80×10^6 cm²) are taken from [27] which was based on a QXAD column. When the model is used with other packing materials and other column dimensions, then values of V_M and A appropriate to the particular system should be used.

Discussion

First the results shown in Figs 2 and 3 will be discussed, then some assumptions implied in the use of the model will be examined, and finally some comments will be made on the significance of this model for ion-pair retention on silica-based alkyl-bonded phases. The data and calculated parameters used to generate Figs 2 and 3 are summarized in Table 1.

Effect of electrolyte

In Fig. 2 it is seen that increasing the total ionic strength c at a fixed concentration of ion-pair reagent in the mobile phase leads to a decrease in the retention of the sample ion. While a larger value of c increases the ion exchange capacity because it increases Γ_P , the value of Γ_P increases at a slower rate than that of c (Table 1). Consequently, from equation (4) it is seen that $k_{S,IEX}^1$ will decrease as c is increased. The effect of c on surface

Table 1
Experimental data from Fig. 1 and parameters for Figs 2 and 3 for an hypothetical sample ion S^{-} *

| $[P^{-}]$ (mol/l) | $[NaCl]$ (mol/l) | c (mol/l) | Γ_P (mol/cm ²) | Q_{weight} (meq/g) | F_P^{AD} (mol/cm ²) | σ_0 (coul/cm ²) | ψ_0 (V) | γ_S | $k_{S,TEX}^*$ | $k_{S,ADS}^*$ | k_S^* |
|----------------------|---------------------|----------------|--------------------------------------|-------------------------|--------------------------------------|---------------------------------------|-----------------|------------|---------------|---------------|---------|
| 0.0025 | 0.011 | 0.0135 | 1.8×10^{-11} | 0.063 | 1.89×10^{-11} | 1.82×10^{-6} | 0.0696 | 0.873 | 384 | 5.3 | 389 |
| 0.0025 | 0.05 | 0.0525 | 2.8×10^{-11} | 0.098 | 2.86×10^{-11} | 2.76×10^{-6} | 0.0645 | 0.764 | 153 | 3.8 | 157 |
| 0.0025 | 0.10 | 0.1025 | 3.5×10^{-11} | 0.123 | 3.53×10^{-11} | 3.40×10^{-6} | 0.0644 | 0.687 | 98 | 3.4 | 101 |
| 0.0025 | 0.25 | 0.2525 | 4.5×10^{-11} | 0.158 | 4.50×10^{-11} | 4.34×10^{-6} | 0.0638 | 0.555 | 51 | 2.7 | 54 |
| 0.0025 | 0.50 | 0.5025 | 5.8×10^{-11} | 0.203 | 5.80×10^{-11} | 5.60×10^{-6} | 0.0695 | 0.436 | 33 | 2.6 | 36 |
| 0.01 | 0.011 | 0.0210 | 3.5×10^{-11} | 0.122 | 3.85×10^{-11} | 3.72×10^{-6} | 0.1029 | 0.844 | 479 | 18.6 | 498 |
| 0.01 | 0.05 | 0.0600 | 5.15×10^{-11} | 0.180 | 5.34×10^{-11} | 5.15×10^{-6} | 0.1034 | 0.750 | 247 | 16.9 | 264 |
| 0.01 | 0.10 | 0.1100 | 6.2×10^{-11} | 0.217 | 6.33×10^{-11} | 6.11×10^{-6} | 0.1039 | 0.678 | 162 | 15.5 | 178 |
| 0.01 | 0.25 | 0.2600 | 7.4×10^{-11} | 0.259 | 7.48×10^{-11} | 7.21×10^{-6} | 0.1001 | 0.555 | 82 | 10.9 | 93 |
| 0.01 | 0.50 | 0.5100 | 9.0×10^{-11} | 0.315 | 9.00×10^{-11} | 8.68×10^{-6} | 0.1041 | 0.433 | 51 | 10.0 | 61 |
| 0.02 | 0.011 | 0.0310 | 5.0×10^{-11} | 0.175 | 5.60×10^{-11} | 5.42×10^{-6} | 0.1230 | 0.810 | 464 | 39 | 503 |
| 0.02 | 0.05 | 0.0700 | 6.9×10^{-11} | 0.242 | 7.28×10^{-11} | 7.02×10^{-6} | 0.1266 | 0.733 | 283 | 41 | 324 |
| 0.02 | 0.10 | 0.1200 | 8.1×10^{-11} | 0.284 | 8.37×10^{-11} | 8.08×10^{-6} | 0.1275 | 0.666 | 194 | 38 | 232 |
| 0.02 | 0.25 | 0.2700 | 9.3×10^{-11} | 0.326 | 9.46×10^{-11} | 9.13×10^{-6} | 0.1218 | 0.544 | 99 | 25 | 124 |
| 0.02 | 0.50 | 0.5200 | 1.13×10^{-10} | 0.400 | 1.13×10^{-10} | 1.09×10^{-5} | 0.1272 | 0.429 | 63 | 24 | 87 |
| 0.04 | 0.011 | 0.0510 | 7.5×10^{-11} | 0.262 | 8.45×10^{-11} | 8.15×10^{-6} | 0.1506 | 0.767 | 420 | 108 | 528 |
| 0.04 | 0.05 | 0.0900 | 9.6×10^{-11} | 0.336 | 1.03×10^{-10} | 9.90×10^{-6} | 0.1559 | 0.704 | 305 | 122 | 427 |
| 0.04 | 0.10 | 0.1400 | 1.07×10^{-10} | 0.374 | 1.13×10^{-10} | 1.09×10^{-5} | 0.1560 | 0.645 | 220 | 113 | 343 |
| 0.04 | 0.25 | 0.2900 | 1.19×10^{-10} | 0.416 | 1.23×10^{-10} | 1.18×10^{-5} | 0.1493 | 0.532 | 118 | 71 | 189 |
| 0.04 | 0.50 | 0.5400 | 1.38×10^{-10} | 0.483 | 1.40×10^{-10} | 1.35×10^{-5} | 0.1526 | 0.423 | 73 | 65 | 138 |
| 0.06 | 0.011 | 0.071 | 9.2×10^{-11} | 0.322 | 1.03×10^{-10} | 9.94×10^{-6} | 0.1619 | 0.732 | 373 | 160 | 533 |
| 0.06 | 0.05 | 0.110 | 1.14×10^{-10} | 0.399 | 1.24×10^{-10} | 1.20×10^{-5} | 0.1743 | 0.678 | 298 | 240 | 538 |
| 0.06 | 0.10 | 0.160 | 1.26×10^{-10} | 0.441 | 1.34×10^{-10} | 1.29×10^{-5} | 0.1748 | 0.626 | 226 | 227 | 453 |
| 0.06 | 0.25 | 0.310 | 1.37×10^{-10} | 0.480 | 1.42×10^{-10} | 1.37×10^{-5} | 0.1673 | 0.521 | 127 | 141 | 268 |
| 0.06 | 0.50 | 0.560 | 1.56×10^{-10} | 0.546 | 1.59×10^{-10} | 1.54×10^{-5} | 0.1703 | 0.416 | 80 | 127 | 207 |

* $K_{S,TEX} = 200$ and $\mu_{S,ADS} = -5 \times 10^3$ joule/mole. Other parameters have values given in the text.

adsorption of S^- is not as marked as its effect on ion exchange, but even in this case an increase in c generally produces a decrease in $k'_{S,ADS}$. The tendency of an increase in Γ_P^{AD} to increase ψ_o is overcome by the tendency of an increase in c to decrease ψ_o (Table 1).

On comparing the several curves in Fig. 2 and examining Table 1, it is evident that a higher concentration of pairing ion in the mobile phase leads to an increase in the relative contribution of surface adsorption compared to that of ion exchange. For the curves obtained at higher $[P^+]$ the decrease in k'_S with increasing c early in the curve is less steep, while the levelling off later in the curve occurs at a higher k'_S value.

Effect of P^+ concentration

From Fig. 3 it is seen that an increase in $[P^+]$ yields an increase in k'_S . This results from an increase in Γ_P in equation (4) and an increase in ψ_o in equation (5). In all these curves c is also increasing to a greater or lesser extent as $[P^+]$ is increased, because in no case is the inert electrolyte completely dominating the ionic strength. However, in the curves measured at a higher concentration of added NaCl (e.g. 0.5 M), c varies less than in curves measured at a lower concentration of added NaCl (e.g. 0.011 M) (Table 1).

For the curve labelled 0.011 M it is precisely the fact that c increases significantly with increasing $[P^+]$ that is responsible for the early steep rise in k'_S , followed by the later levelling off. This can be seen in Table 1. If the five rows for which $[NaCl] = 0.011$ M are compared, the quantity $k'_{S,IEX}$ is the major contributor to k'_S . From equation (4) it is clear that the columns of primary interest in these five rows are those headed c and Γ_P . Note that a 1.6-fold change in c from 0.0135 to 0.021 M produces a 1.9-fold increase in Γ_P . This accounts for the early jump in k'_S . In the intermediate range of c , both c and Γ_P are changing at about the same rate, causing the curve to flatten out. At high values of c , a 1.4-fold change from 0.051 to 0.071 M produces only a 1.2-fold change in Γ_P . This is responsible for a decrease in $k'_{S,IEX}$ at high c . Thus a plot of $k'_{S,IEX}$ vs $[P^+]$ for $[NaCl] = 0.011$ M would pass through a maximum. It is only the fact that $k'_{S,ADS}$ increases monotonically over the whole range of c that prevents a maximum from appearing in the plot of k'_S vs $[P^+]$.

Evidently, if a different sample S^- were being considered for which a smaller value of $\mu_{S,ADS}^o$ applied, then the contribution of $k'_{S,IEX}$ to k'_S would be relatively greater and a maximum would appear in the k'_S plot. Furthermore, the maximum would be even more pronounced if the NaCl concentration were even lower than 0.011 M. Finally, if the experimentally measured isotherm for the pairing ion P^+ were to show marked flattening at higher values of $[P^+]$, then plots of k'_S vs $[P^+]$ would be certain to show a pronounced maximum *under non-swamping conditions*, because Γ_P would stop increasing while c would continue to increase at concentrations corresponding to the flat part of the P^+ isotherm.

Assumptions

The term *adsorption* has been used above when referring to the sorption of P^+ and S^- onto the surface. Depending upon their view of the structure of the alkyl chains in a bonded-phase packing, some workers might take exception to the use of this term. The difference is semantic — the point is that it is well established that P^+ is sorbed onto alkyl-bonded phases. However one wishes to describe the process responsible for the sorption of P^+ , the same kind of process can be invoked for the sorption of S^- . The double-layer model described herein is still valid.

The significance of the surface activity coefficient $\gamma_{S,ADS}$ should be clarified.

Essentially, the SGC theory is a means of taking into account a 'surface ionic activity correction', quite analogous to the way in which the Debye–Hückel theory takes into account the 'solution ionic activity correction'. The quantity $\gamma_{S,ADS}$, on the other hand, is not at all related to ionic effects or electrical potential. It is a 'correction' term to take into account the fact that the value of the *chemical* potential for the sorption of S^- from bulk solution onto the surface may change when the character of the surface changes.

Changes in surface character can be due to different degrees of coverage by P^+ . Thermodynamically, $\gamma_{S,ADS}$ corrects for the fact that $\mu_{S,ADS}^0$ is always defined using a hypothetical surface with an infinitely low P^+ surface excess as the thermodynamic reference state, while in fact experiments are performed on surfaces with various and finite values of Γ_P^{AD} . The best analogy in solution chemistry is the 'transfer activity coefficient', which must be used when dealing with solutes dissolved in mixed aqueous–organic solvents, while taking infinite dilution in water as the reference state [32]. For simplicity, and because it has been specified that only a small fraction of the surface is occupied by P^+ , it has been assumed that $\gamma_{S,ADS} \approx 1$. At higher surface coverage by P^+ the magnitude of the chemical forces of surface adsorption of S^- might be expected to change, causing $\gamma_{S,ADS}$ to vary from 1. The experimental evaluation of $\gamma_{S,ADS}$ is not easy. It might be estimated from changes in sorption of a neutral sample component with changes in Γ_P^{AD} .

An implicit assumption in equation (1) is that the adsorbed PCl is fully 'dissociated' so that there is no Cl^- closer to the surface than the outer Helmholtz plane. In SGC terms this means that Cl^- is not 'specifically adsorbed' [23]. For adsorption of DPGHCl this assumption appears to be justified [23]. In cases where adsorbed PCl is not fully dissociated then the non-dissociated PCl should not be included in the value of Γ_P^{AD} .

Comments and Conclusion

Many workers now talk about 'dynamic' ion exchangers created by the sorption of P^+ and also recognize that the sample ion S^- may be sorbed to some extent in the absence of an ion-pair reagent. However, there appears to have been very little recognition of the role played by the surface potential created by the sorption of P^+ in *enhancing* the surface sorption of S^- [23, 27]. The relative contributions of ion exchange in the diffuse layer and surface adsorption to the overall k'_S must, of course, be experimentally evaluated for any real situation. In the example discussed above only one family of experimental isotherms (i.e. for $DPGH^+$) was discussed and only one set of values of $K_{S,IEX}$ and $\mu_{S,ADS}^0$ was used for illustration. The values of $K_{S,IEX}$ and $\mu_{S,ADS}^0$ can vary independently of one another among a group of sample ions.

The shape of the sorption isotherm for P^+ is especially important in determining the shape of the plots of k'_S vs c and of k'_S vs $[P^+]$. The P^+ isotherm should be experimentally measured.

When aqueous–organic solvent mixtures are used instead of water for preparing the mobile phase, the values of many parameters in the equations will be different. Furthermore, not only would Γ_P^{AD} , but also the amount of organic solvent sorbed from the mobile phase onto the packing material would be expected to change with changing c and $[P^+]$. This introduces an even greater dependence of parameters such as $\gamma_{S,ADS}$ and $K_{S,IEX}$ on mobile phase composition. Nevertheless, the double-layer adsorption and exchange model still applies.

A perennial complicating factor in retention studies in ion-pair chromatography is the

existence of residual silanol groups on the reversed-phase bonded packing [15, 21, 26]. At all but low pH these are ionized, creating a negative surface charge. Their degree of ionization is greater at higher pH. When a P^+ pairing ion is sorbed onto a reversed-phase bonded packing that possesses anionic silanolate sites, the value used for Γ_P should be lower than the value measured experimentally by the moles cm^{-2} of silanolate sites.

It has been shown above how a maximum in the plot of k'_S vs $[P^+]$ can occur when the ionic strength of the mobile phase is not dominated with an inert electrolyte. This is not to imply that other conditions are unable to cause such maxima. In particular, when the concentration of a surface-active P^+ in the mobile phase exceeds its critical micelle concentration, such maxima can be expected to occur.

The case in which the pairing ion is negatively charged and the sample ion positively charged can be treated in a completely analogous manner, with appropriate sign reversals, to that discussed above. Also, the case in which pairing ion and sample ion have the same sign of charge can be described by an extension of the treatment used for co-ion sorption on a low capacity ion exchanger [27].

Recently some empirical observations on the effect of electrolyte concentration and ion-pair reagent concentration on the retention of a sample ion have been summarized [33]. It would appear that all of the phenomena described therein, as well as the phenomena that have been described over the last several years in studies of ion-pair chromatography, are consistent with the double-layer adsorption and exchange model elaborated in the present paper. Naturally, quantitative experimental testing of the model is required. Such tests are presently underway in this laboratory, employing experimental techniques similar to those used in testing the model on low capacity ion exchangers [27, 28].

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Appendix

Γ_P^{AD} versus Γ_P

The distinction between Γ_P^{AD} and Γ_P arises from the fact that the positive charge on the surface due to adsorbed P^+ is balanced by some combination of both a positive surface excess of Cl^- counterions in the diffuse layer Γ_-^{DL} , and a negative surface excess (i.e. deficiency) of positively charged co-ions, Na^+ and P^+ , in the diffuse layer Γ_+^{DL} . The value of Γ_+^{DL} is negative. The calculation of Γ_P^{AD} and ψ_0 from the experimentally measured Γ_P requires an iterative calculation, for which the steps are outlined below [23, 34].

(i) First the approximation is made:

$$\Gamma_P^{AD} \approx \Gamma_P \quad (a)$$

(ii) Then σ_0 is calculated from equation (1).

(iii) The value of the electrical potential at the outer Helmholtz plane, ψ_{OHP} , is calculated via the expression:

$$\sinh\left(\frac{Z_+ F \psi_{OHP}}{2RT}\right) = 8.53 \times 10^4 \sigma_0 \sqrt{c} \quad (b)$$

The value of the argument in the hyperbolic sinh term can be found in tables [35].

(iv) Having a first approximation of ψ_{OHP} from equation (b), the ratio of the negative surface excess of co-ions to the positive excess of counterions in the diffuse layer can be calculated at 25°C as:

$$\frac{\Gamma_+^{DL}}{\Gamma_-^{DL}} = \frac{\exp[-19.47 \psi_{OHP}] - 1}{\exp[19.47 \psi_{OHP}] - 1} \quad (c)$$

This quantity has a negative value because Γ_+^{DL} is negative.

(v) A better estimate of σ_o can now be obtained from the expression

$$\sigma_o = Z_+ F \Gamma_P \left[\frac{\alpha - R}{\alpha - R(1-\alpha)} \right] \quad (d)$$

where α is the fraction of all counterions represented by P^+

$$\alpha = [P^+]/c \quad (e)$$

and R is the ratio of negative surface excess of P^+ co-ions to the total positive surface excess of counterions

$$R = \frac{\Gamma_+^{DL}}{\Gamma_-^{DL}} \cdot \alpha. \quad (f)$$

R has a negative value because $\Gamma_+^{DL}/\Gamma_-^{DL}$ is negative. (Note: Both equations (28) and (29) in [23] have errors of sign, which, however, cancel out to give the correct result.)

(vi) The new estimate of σ_o from equation (d) is used iteratively in steps (iii)–(v) until constant values of Γ_P^{AD} and σ_o are obtained. In the present case one iteration was found to be sufficient and the difference between Γ_P^{AD} and Γ_P was never more than about 15% (Table 1).

(vii) With the final values of σ_o and ψ_{OHP} , the value of the surface potential is next calculated from

$$\psi_o = \frac{\sigma_o}{C_1} + \psi_{OHP} \quad (g)$$

where C_1 is the capacitance of the compact part of the double layer given by

$$C_1 = \frac{\epsilon}{4\pi d} = 1.5 \times 10^{-4} \text{ Farad/cm}^2. \quad (h)$$

(viii) The resultant value of ψ_o is used in equation (5) to calculate $k'_{S,ADS}$.

When the mobile phase contains a dominant or 'swamping' concentration of inert electrolyte (i.e. $c \approx [\text{NaCl}]$) then $\alpha \ll 1$ and equation (d) is identical to equation (1), or $\Gamma_P^{AD} = \Gamma_P$.

Equation for $k'_{S,IEX}$

In previous studies in which low capacity ion exchangers were investigated [27, 28, 30], the denominator of equation (4) featured a factor of 2. This compensated for the negative excess (or 'electrolyte exclusion') effects by using a 'low-potential' approximation. When $\psi_{OHP} \leq 0.025$ V, then $\Gamma_+^{DL}/\Gamma_-^{DL} \approx -1$; or about half of the surface excess in the diffuse layer is compensated as a negative excess. In the present case the negative excess correction is implicit in the experimentally measured value Γ_P , so that no extra correction is needed and the factor 2 is therefore absent from equation (4).